

Description

Ceramic Multi-Layer Component And Method For The Production Thereof

5 The invention relates to a multilayer ceramic component comprising a stack of alternating ceramic layers and copper-containing electrode layers, which serve as internal electrodes, wherein the internal electrodes are connected to external contacts that are arranged on opposite, exterior sides of the stack, perpendicular to the multilayer structure, and wherein the internal electrodes that are connected to different external contacts are in
10 interlocking engagement with one another. A component of this type and a method for its production are known, for example, from the publication DE 20023051.4.

 The invention further relates to a method for producing the above-named multilayer component.

15 From the publication DE 9700463 a method for producing green films for multilayer piezoceramic components with Ag/Pd internal electrodes is known, in which a PZT-type piezoceramic powder (PZT = lead zirconate titanate) is used.

20 The material and/or the process used to fire on the external electrodes that are contacted to the internal electrodes should in principle be selected such that the electrode

metal will not oxidize and the ceramic will not be reduced. For this reason a precious metal or a precious metal alloy is customarily used as the electrode material.

5 In the publication DE 19945933, for example, a method for producing external electrodes in piezoceramic components comprised of PZT ceramic and Ag/Pd internal electrodes is described. The contacting of the Ag/Pd internal electrodes is accomplished using a metal paste that has a silver content of > 65 % and an organic binder, which is fired on at approximately 700° C. The firing on of the metal paste is conducted in an air atmosphere, because aromatic compounds contained in the organic paste binder cannot be
10 completely degraded under reductive conditions. However this method is not suited to a multilayer component with PZT ceramic and copper-containing internal electrodes, since at customary debinding and/or firing-on temperatures reduction of the PZT ceramic and oxidation of the metallic copper are prevented under only one specific, very low oxygen partial pressure of < 10⁻² Pa. Thus the Ag/Pd external electrodes cannot be used in a
15 multilayer ceramic component with copper-containing internal electrodes.

With a component known from the publication DE 20023051 U1 it is possible to avoid the high cost disadvantage of multilayer piezoceramic components based on a PZT ceramic and Ag/Pd internal electrodes by using copper-containing internal electrodes in
20 place of the expensive Ag/Pd internal electrodes. However this publication does not indicate which material would be suitable for firing on external electrodes in a piezoceramic component with copper-containing internal electrodes.

The object of the invention is to disclose a multilayer ceramic component with internal electrodes and external contacts for contacting the internal electrodes, in which the bonding strength of the external contacts is sufficient, and a method for producing said
5 component, in which the ceramic is not reduced and in which neither internal nor external electrodes will oxidize.

The object of the invention is attained with a component of the type described at the beginning having the characterizing feature disclosed in claim 1, and with the process
10 according to claim 11.

The invention discloses a multilayer ceramic component comprising a stack of alternating ceramic layers and copper-containing electrode layers that serve as internal electrodes, wherein the internal electrodes are connected to external contacts. The
15 external contacts are arranged on exterior surfaces of the stack, opposite one another and perpendicular to the multilayer structure, wherein the internal electrodes that are connected to different external contacts are in interlocking engagement with one another. The multilayer component is characterized in that the external contacts contain metallic copper, wherein the bonding strength of the external contacts to the stack amounts to at
20 least 50 N.

The ceramic layers are preferably comprised of ceramic green films that contain a thermohydrolytically degradable binding agent and can comprise a ferroelectric perovskite ceramic of the general composition ABO_3 , especially one of the PZT type $Pb(Zr_xTi_{1-x})O_3$.

5 The invention further discloses a method for producing a component as specified in the invention, in which the binder removal, or debinding, is performed and/or completed at a temperature of $\leq 300^\circ \text{C}$. The debinding takes place under a nitrogen stream with the addition of water vapor, wherein the water vapor partial pressure is set such that the corresponding oxygen partial pressure at the given temperature lies between
10 the equilibrium points for $\text{Cu}/\text{Cu}_2\text{O}$ and PbTiO_3/Pb . The equilibrium point corresponds to an oxygen partial pressure at which both a reduced metal and a metal compound that corresponds to this metal are thermodynamically stable and can coexist without diffusing into one another.

15 According to the invention, the paste binders are completely separated out in a reduced atmosphere of, for example $< 10^{-2} \text{ Pa}$ at a comparatively low temperature of $\leq 300^\circ \text{C}$, because at higher debinding temperatures the oxygen, which is insufficient to burn off the carbon contained in the organic binder, is partially drawn out of the ceramic lattice structure, which impairs the properties of the ceramic layers.

20 A complete separation of organic constituents is enabled according to the invention in that the debinding is performed in a nitrogen stream that is charged with

water vapor, resulting in hydrolytic separation. The addition of the water vapor causes the oxygen partial pressure to decrease thermodynamically, however the oxygen partial pressure does not drop below a specific level at which the ceramic would begin to reductively degrade.

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On the other hand, the oxygen partial pressure also will not exceed a certain level at which the metallic copper would begin to oxidize at the given temperature.

Thus the oxygen partial pressure is selected to be low enough that the reduction processes in the ceramic remain adequately inhibited, while at the same time the copper contained in the metal paste will not oxidize.

The oxygen partial pressure is maintained or correspondingly adjusted at all times to correspond to the temperature, not only during the debinding process but also during firing on of the metal paste, such that in the $p(T)$ diagram it lies between the equilibrium points for Cu/Cu_2O and Pb/PbO at each process temperature.

The proportion of copper in the metal paste is preferably $> 70\%$. Acrylic resin binders are preferably used as the organic paste binders.

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The invention makes it possible to use a (copper-containing) metal paste with an organic paste binder to produce external contacts in a piezoceramic component with internal electrodes that contain copper.

5 To produce the external contacts, a copper-containing metal paste having a copper content of > 70 m%, for example 78 m%, a glass flow, and an organic binder, for example acrylic resin binder, are preferably used.

10 The glass flow (glass frit) is preferably comprised essentially of PbO and SiO_2 , but may also contain other components, for example Na_2O , Al_2O_3 and BaO . The proportion of the glass flow in the metal paste is preferably less than 5 m%. The composition and the proportion of the glass flow are selected such that the glass frit contained in the metal paste of the external contacts partially diffuses into the ceramic, thereby increasing the bonding strength of the external contacts to the sides of the stack.

15 First, using a known process, a stack consisting of electrode layers placed one on top of another, which in a finished component correspond to the internal electrodes, and layers of a ceramic material is produced. The electrode layers are comprised of a copper-containing metal paste and can be applied to the layers made of a ceramic material, for
20 example, by means of screen printing.

The copper-containing metal paste is also applied, for example via screen printing, on opposite sides of the stack of internal electrodes and ceramic layers, which are positioned one on top of another.

5 The binder is removed from the metal paste in a moist nitrogen atmosphere in a gas-tight furnace at a temperature of $\leq 300^{\circ}\text{C}$, after which it is sintered at a higher temperature.

10 The copper-containing metal paste is preferably fired on at between 700 and 860°C .

To prevent the reduction of the lead oxide contained in the ceramic, lattice bases made of metallic copper, which serve simultaneously as gettering material, can be used in the production of a component as specified in the invention.

15 Below, the invention will be described in greater detail with reference to exemplary embodiments and the associated drawings. The figures contain schematic, not to scale representations of various exemplary embodiments of the invention. Identical or equivalent components are assigned the same reference figures. The drawings show

20 Figure 1 a perspective view of the structural design of a component of the invention

Figure 2 a half-logarithmic representation of oxygen partial pressure, which can be adjusted via the addition of water vapor, as a function of the temperature and the equilibrium curves for Cu/Cu₂O and Pb/PbTiO₃.

5 In Figure 1 a ceramic component with copper-containing external contacts AK1 and AK2 as specified in the invention is schematically illustrated. First copper-containing internal electrodes IE1 are connected to the first external contact AK1. Second copper-containing internal electrodes IE2 are connected to the second external contact AK2. The internal electrodes are separated from one another by ceramic layers KS.

10 The ceramic layers KS preferably possess piezoelectric properties and are produced, for example, using the PZT-type ceramic.

15 The component shown here specifically represents a piezoelectric actuator. The electrode layers and ceramic layers stacked one on top of another are referred to as a piezo stack.

20 The fired-on external contacts AK1, AK2 are preferably between 10 and 20 μm, for example 15 μm, thick. However a different thickness for the external contacts may also be chosen.

The external contacts and/or internal electrodes preferably contain a certain proportion of ceramic, which preferably is less than 50 m% (m% - percentage by mass), which in one preferred variant of the invention is between 10 and 50 m%, and which especially amounts to 40 m%. In this, the ceramic proportion comprises ceramic particles
5 having a specific grain size, for example an average grain size of between 0.2 and 0.6 μm .

The ceramic portion in the metal paste serves especially to inhibit the formation of cracks and the separation of the external contact from the piezo stack, which can result from the different expansion properties of the ceramic material and the metallic copper.
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The thermal expansion coefficient of the PZT-type ceramic within the temperature range extending from room temperature to the Curie temperature is approximately 1.5 - 2.0 ppm/K, while within the same temperature range metallic copper demonstrates a substantially higher thermal expansion coefficient of approximately 19 ppm/K. By
15 admixing the ceramic material into the metal paste the expansion characteristics of the external contact are adjusted to the expansion behavior of the ceramic stack both for the processing of the component and for its later applications within the specified temperature range of, for example, -50° C to +150° C, wherein, for example, the application of an electrical field causes a deformation of the component.
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To adjust the thermal expansion coefficient, a glass frit that contains a high proportion of SiO_2 , for example 39 m%, is preferably used, since SiO_2 has a high affinity for PZT-type ceramic.

5 In the preparation of the copper-containing metal paste, first a ceramic powder having an average grain size of, for example, $0.4 \mu\text{m}$ is dispersed in a solvent. The ceramic powder dispersion is then stirred into the copper-containing metal paste of the above-named composition, and is homogenized using a three-roller drawing machine. The viscosity of the metal paste preferably amounts to between 10 and 20 Pas. Once the
10 finished metal paste has been applied to the side surfaces of the piezo stack, the paste is dried at approximately 80 to 140°C in an air atmosphere. This is followed by a debinding and sintering under the conditions specified in the invention, in which the oxidation of the metallic copper and the reduction of the PbO or PbTiO_3 are prevented. In this, especially in the selection of the debinding temperature and the duration of the
15 debinding process, the focus is on ensuring that during the debinding process both the binder components and the residual solvent will be completely burned out of the metal paste.

Because the glass frit contained in the metal paste can diffuse quite extensively
20 into the ceramic, leaving behind hollow cavities in the sintered ceramic layers, the sinter temperature is selected to be low enough (for example 765°C) that the glass additive can penetrate only in the area of the internal electrodes. Microscopic studies have shown that

at such a sinter temperature glass portions, above all silicon oxide, can be detected only within a narrow area of the ceramic layers that is adjacent to the external contacts. The external contacts adhere firmly and can be detached from the piezo stack only with the application of a high level of force, greater than 50 N. With the forceful detachment of the external contacts, portions of the ceramic material are broken off, which indicates a high level of bonding strength for the external contacts on the piezo stack.

The ceramic proportion preferably amounts to 40 m% relative to the solids content of the metal paste. In principle this metal paste can also be used for internal electrode layers.

It is also within the scope of the invention to use a preferably chemically active ceramic powder (or even some other chemically active additive), hereinafter also referred to as a ceramic additive, in the electrode metallization, which under certain circumstances can react chemically with the electrode metal, the organic binder, the ceramic, and/or a reaction product of the latter, or can chemically bind certain components. Furthermore, the ceramic additive can react with the process atmosphere, for example it can release the oxygen into the process atmosphere or conversely can absorb it, whereby the oxygen partial pressure is stabilized at least locally or temporarily. With a stable oxygen partial pressure it is possible especially to protect the internal electrode layers or the external contacts from oxidation and to protect the ceramic layers from reduction. The ceramic powder additive ensures that a metal oxide that has been formed as a result of process

instabilities in the electrode metallization is bonded, thus preventing an undesirable diffusion of this metal oxide into the ceramic layers.

5 The process of using a chemically inert ceramic powder in a metal paste, for example to retard the sintering of the metal, is known in the art. According to the invention, however, the ceramic powder is used as a functional additive that is chemically active and can chemically react with its environment. The chemical activity can be focused, for example, on the binding of Pb, which is released from the lead-containing ceramic material during sintering. It is also possible for the chemically active ceramic
10 powder to bind another component from the ceramic mass especially during sintering, or to promote the release of certain components such as, for example, oxygen from the ceramic mass or from the binder contained in the ceramic mass or in the metal paste. It is a requirement, however, that the ceramic powder will not chemically react with the metal portion of the metal paste.

15 In contrast to the metal paste that is used for the external electrodes, in the metal paste that is suitable for use in the internal electrode layers preferably no glass additives are used. $(Zr,Ti)O_2$ is particularly well suited for use as the chemically active ceramic powder. In place of a chemically active ceramic powder the metal paste can also contain
20 another chemically active additive, or in addition to the chemically active ceramic powder it may contain portions of other substances, for example BaO_2 and/or MgO .

The addition of a ceramic powder in the case of the internal electrodes further serves to improve adhesion between the internal electrodes and the ceramic layers that surround them, wherein a fine distribution of the ceramic particles among the metal particles especially serves to prevent sinter neck formation. The sinter necks represent a localized disconnection of the internal electrodes, in which the metal coating becomes detached from the ceramic layer and/or becomes pulled back - especially around the edges - so that the internal electrodes assume a net-like structure, which is not replicable from component to component. The method of achieving a homogeneous internal electrode structure by adding a precious metal or a precious metal alloy is known in the art. However the addition of the ceramic powder as specified in the invention also provides a substantial cost advantage relative to this known method.

Figure 2 shows a half-logarithmic representation of an oxygen partial pressure p_{O_2} that can be adjusted based upon the temperature - according to the invention by adding water vapor - and is illustrated by way of example by the curve 3, the numerically calculated equilibrium curve 1 for Cu and Cu_2O , and the numerically calculated equilibrium curve 2 for Pb and $PbTiO_3$.

The equilibrium curve 1 indicates the partial pressure of O_2 at the selected temperature, at which metallic Cu and Cu_2O can coexist. Metallic copper exists only at an oxygen partial pressure p_{O_2} that does not exceed the equilibrium level, i.e. below the equilibrium curve 1. Because only Cu_2O is stable above the curve 1, at an oxygen partial

pressure that exceeds the equilibrium value at the selected temperature an undesirable oxidation of the metallic copper will occur.

The equilibrium curve 2 indicates the partial pressure for O_2 at the selected
5 temperature, at which metallic Pb and $PbTiO_3$ can coexist. $PbTiO_3$ exists only above the curve 2. At an oxygen partial pressure p_{O_2} that drops below the equilibrium level at the selected temperature, the $PbTiO_3$ contained in the ceramic will be reduced to Pb.

For this reason, at least during the debinding phase of a process of the invention
10 for producing a multilayer ceramic component, the oxygen partial pressure p_{O_2} is adjusted by adding water vapor such that it does not exceed the maximum level p_{max} as defined by the curve 1, at which metallic copper is still stable, but also will not drop below the minimum level p_{min} as indicated by the curve 2, at which lead titanate is not yet reduced, i.e. $p_{min} < p_{O_2} < p_{max}$ at the given debinding temperature T_E . The permissible range for
15 adjustment of the oxygen partial pressure thus lies between the curves 1 and 2.

The curve 3 describes an optimal oxygen partial pressure as defined by the invention, to be established based upon temperature and within a moist atmosphere. The quantity of water vapor to be added can be calculated in principle from the curve 3. It is
20 also possible to manually or automatically control the drop in the oxygen partial pressure by adding water vapor, in such a way that the preset threshold values are not exceeded.

List of Reference Figures

	1	Characteristic curve for the equilibrium of Cu and Cu ₂ O in the diagram $\log\{p(O_2)\}$ plotted against temperature
5	2	Characteristic curve for the equilibrium of Pb and PbTiO ₃ in the diagram $\log\{p(O_2)\}$ plotted against temperature
	3	Characteristic curve for oxygen partial pressure, adjusted via the addition of water vapor, as a function of temperature
	AK1, AK2	External contact
10	KS	Ceramic layer
	IE1	Internal electrodes connected to the external contact AK1
	IE2	Internal electrodes connected to the external contact AK2
	P _{O2}	Oxygen partial pressure
	P _{min}	Minimum permissible oxygen partial pressure
15	P _{max}	Maximum permissible oxygen partial pressure
	T _E	Debinder temperature